Chem 116 Lecture 13
10/16/08 (SI)

Kinetics
Study of rates of chemical reactions

Today's agenda
Modeling of kinetics at particle level
Collision theory
Arrhenius Equation/ prediction of temperature dependence /k
Reaction mechanisms
The use of experimental data to determine rate laws:
Special case by case analysis/ first order rate laws
Completing the table

Half life
This is the amount of time it takes for a half of the reactant to disappear (or react)
There are two ways of doing this: via a mathematical equation or graphically.
The mathematical equation is;
$[A]_t$ is a function of t
For a first order reaction $[A]_t$ is given by $\ln [A]_t = \ln [A]_0 - kt$
Half life is the value of t when $[A]_t = ½[A]_0$

A half life graph could be plotted as concentration against time, but that isn't linear. What is linear (straight line with negative slope) is $\ln [A]_t$ against time

There are two general equations for half life if the reaction is a first order:
1) integrated rate law and
2) the differential rate law.

Integrated rate law: $\ln [A]_t = \ln [A]_0 – kt$
The differential rate law: Rate = $\Delta[A]/ \Delta t = k [A]$
If k is known, we can solve the equation algebraically, but it is usually easier to work with half life equations

All nuclear decay processes are first order as explained in class.

What happens at the particle level in relation to the reaction rates
The more the reactant particles, the more collisions
When the average speeds of reactants increase, they collide more often and there must be an explanation for this at the particle level.
In conclusion, for particles to react with each other, they have to collide

Factors affecting reaction rates at the macroscopic level:
Increase in the concentration of the reactants leads to increased rate of reaction

Increase in temperature of the reaction increases the rate of reaction
Different reactions can have very fast or very slow reaction rates, even when they have the same form of the rate law - in this case what matters is the value of k. If k is smaller, then the rate is slower. If k is larger then the rate is faster.

In conclusion, rate laws always have the mathematical form:

$$\text{Rate} = k\,[A]^n\,[B]^m$$

The theoretical form for the basis of rate law depends on how particles behave (we'll get to mechanisms next lecture), which is what determine the $[A]^n\,[B]^m$ part. The things that determine the k part are temperature, the activation energy, and the fraction of collisions that happen at the right orientation for the reaction to occur.

Factors affecting the rate law:
Temperature; must be in Kelvin (K)
Number of particles related to concentration of the reactants and something that can explain why two reactions with same *T* can have different values of k